

**ESPERANZAITE, $\text{NaCa}_2\text{Al}_2(\text{As}^{5+}\text{O}_4)_2\text{F}_4(\text{OH})\cdot 2\text{H}_2\text{O}$,
A NEW MINERAL SPECIES FROM THE LA ESPERANZA MINE, MEXICO:
DESCRIPTIVE MINERALOGY AND ATOMIC ARRANGEMENT**

EUGENE E. FOORD¹

United States Geological Survey, MS 905, Box 25046, Denver Federal Center, Lakewood, Colorado 80225, U.S.A.

JOHN M. HUGHES²

Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

FORREST CURETON

21267 Brewer Road, Grass Valley, California 95949, U.S.A.

CHARLES H. MAXWELL

950 Allison Street, Lakewood, Colorado 80215-5942, U.S.A.

ALEXANDER U. FALSTER

Department of Geology and Geophysics, University of New Orleans, New Orleans, Louisiana 70148, U.S.A.

ANDRE J. SOMMER

Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056, U.S.A.

PAUL F. HLAVA

Department 1822, MS-1405, Sandia National Laboratories, Albuquerque, New Mexico 87185-1405, U.S.A.

ABSTRACT

Esperanzaitite, ideally $\text{NaCa}_2\text{Al}_2(\text{As}^{5+}\text{O}_4)_2\text{F}_4(\text{OH})\cdot 2\text{H}_2\text{O}$, $Z = 2$, is a new mineral species from the La Esperanza mine, Durango State, Mexico. The mineral occurs as blue-green botryoidal crystalline masses on rhyolite, with separate spheres up to 1.5 mm in diameter. The Mohs hardness is $4\frac{1}{2}$, and the specific gravity, 3.24 (obs.) and 3.36(3) (calc.). Optical properties were measured in 589 nm light. Esperanzaitite is biaxial (-), $X = Y = Z =$ colorless, α 1.580(1), β 1.588(1), and γ 1.593(1); $2V_{\text{obs}}$ is $74(1)^\circ$ and $2V_{\text{calc}}$ is 76.3° . The dispersion is medium, $r < v$, and the optic axes are oriented according to $a \wedge Z = +50.5^\circ$, $b = Y$, $c \wedge X = +35^\circ$. The strongest five X-ray-diffraction maxima in the powder pattern [d in $\text{\AA}(I)(hkl)$] are: 2.966(100)(13 $\bar{1}$, 31 $\bar{1}$, 031), 3.527(90)(220), 2.700(90)(221,002,040), 5.364(80)(001,020) and 4.796(80)(011). Esperanzaitite is monoclinic, a 9.687(5), b 10.7379(6), c 5.5523(7) \AA , β 105.32(1) $^\circ$, space group $P2_1/m$. The atomic arrangement of esperanzaitite was solved by direct methods and Fourier analysis ($R = 0.032$). The Fundamental Building Block (FBB) is formed of [001] stacks of heteropolyhedral tetramers; the tetramers are formed of two arsenate tetrahedra and two Al octahedra, corner-linked in four-member rings. The FBBs are linked by irregular $\text{Na}\phi_5$ and $\text{Ca}\phi_8$ polyhedra.

Keywords: esperanzaitite, new mineral species, crystal structure, La Esperanza mine, Durango, Mexico.

SOMMAIRE

La esperanzaitite, dont la composition idéale serait $\text{NaCa}_2\text{Al}_2(\text{As}^{5+}\text{O}_4)_2\text{F}_4(\text{OH})\cdot 2\text{H}_2\text{O}$, $Z = 2$, est une espèce minérale nouvelle découverte à la mine La Esperanza, dans l'état de Durango, au Mexique. Il s'agit d'un minéral bleu-vert se présentant en amas

¹ Deceased January 1998.

² E-mail address: hughesjm@muohio.edu

reniformes de cristaux sur la rhyolite, les sphères distinctes atteignant 1.5 mm de diamètre. La dureté de Mohs est $4\frac{1}{2}$, et la densité, 3.24 (observée) et 3.36(3) (calculée). On a déterminé les propriétés optiques avec une illumination à 589 nm. La esperanzaïte est biaxe négative, $X = Y = Z =$ incolore, α 1.580(1), β 1.588(1), et γ 1.593(1); $2V_{\text{obs}}$ est $74(1)^\circ$, et $2V_{\text{calc}}$ est 76.3° . La dispersion est modérée, $r < v$, et les axes optiques sont orientés selon $a \wedge Z = +50.5^\circ$, $b = Y$, $c \wedge X = +35^\circ$. Les cinq raies les plus intenses du cliché de diffraction, méthode des poudres [d en Å(I)(hkl)], sont: 2.966(100)(13 $\bar{1}$, 31 $\bar{1}$, 031), 3.527(90)(220), 2.700(90)(221,002,040), 5.364(80)(001,020) et 4.796(80)(011). La esperanzaïte est monoclinique, a 9.687(5), b 10.7379(6), c 5.5523(7) Å, β 105.32(1) $^\circ$, groupe spatial $P2_1/m$. L'agencement des atomes a été déterminé par méthodes directes et par analyse de Fourier jusqu'à un résidu R de 0.032. Le module structural fondamental est un empilement le long de [001] de tétramères hétéropolyédriques; ces tétramères sont formés de deux tétraèdres d'arsenate et deux octaèdres d'Al, à coins partagés, en anneaux à quatre membres. Ces modules sont liés par des polyèdres NaO_5 et CaO_8 irréguliers.

(Traduit par la Rédaction)

Mots-clés: esperanzaïte, nouvelle espèce minérale, structure cristalline, mine La Esperanza, Durango, Mexique.

INTRODUCTION

The La Esperanza mine is located in the Zaragoza mining district, 3.7 km southeast of the village of Madero, located in the State of Durango 60 km north-east of Durango, Mexico. The mine is hosted in a tin-bearing rhyolite, which has yielded minor amounts of vein cassiterite as ore. During a visit to the mine, one of us (CHM) noticed a botryoidal blue-green mineral on an ore pile located several meters from the main shaft. Samples were collected, and were subsequently examined by many investigators over the past 15 years. The recent solution of the crystal structure clarified many of the analytical ambiguities that vexed the senior author for over a decade; his coauthors are pleased that the work came to fruition in time that Gene could view the structure before his untimely death.

The mineral and mineral name, esperanzaite, have been approved by the IMA-CNMMN. Esperanzaite is named after the mine at which it was found. A portion of the type specimen has been deposited at the United States National Museum, Smithsonian Institution (NMNH 171530), and in the collection of Forrest Cureton. Only a few grams of esperanzaite exist; one of the authors (FC) returned to the site after the original discovery, but no additional material was found.

PHYSICAL PROPERTIES

Esperanzaite occurs as botryoidal pale blue-green (seafoam green) patches up to 0.8 cm across and separated spheres up to 1.5 mm in diameter of radiating crystals on a single sample of altered rhyolite. Associated minerals include hematite, cassiterite, quartz, tridymite, cristobalite, opal, calcite, zeolites, mimetite, and clay minerals (unidentified). The mineral displays a vitreous luster and a white streak, and is transparent to translucent. No fluorescence was observed in short- or long-wave ultraviolet radiation.

Esperanzaite can scratch fluorite but would not scratch apatite, thus its Mohs hardness is approximately $4\frac{1}{2}$. No parting was observed; however, a perfect cleavage parallel to the c axis is evident. The phase has brittle

tenacity. The density was measured as 3.24 g/cm^3 (Berman balance) on 12.2 mg of impure material, and calculated as $3.36(3) \text{ g/cm}^3$ from the ideal formula and observed cell.

A thermogravimetric analysis on 3.1 mg of material was undertaken over the interval 25° to 1000°C . A total of 16 wt.% was lost, 10% at 450° , and the remainder, to 1000°C . Infrared analysis of the sample was conducted with a Harrick split-pea attenuated total internal reflection (ATR) accessory interfaced to a Perkin Elmer Spectrum 2000 Fourier Transform Infrared Spectrometer (FTIR). A single crystal of esperanzaite approximately 200 μm in diameter was flattened into a pellet with a hand press. Spectra were collected at 4 cm^{-1} resolution combining a total of 32 individual scans.

The infrared spectrum is shown in Figure 1. Prominent absorptions can be observed at 3435, 1615, 1175, 844 and 832 cm^{-1} . Vibrational assignments of these absorptions include: O–H stretching at 3435 and 3246 cm^{-1} (two different forms of hydrogen bonding), H–O–H stretch at 1614 cm^{-1} (lattice H_2O), Al–O–H stretch at 1173 cm^{-1} , and the ν_3 asymmetric stretch of a tetrahedral polyatomic cluster at 844 and 832 cm^{-1} (AsO_4^{3-} anionic complex).

Optical properties of esperanzaite were measured at 589 nm. The phase is biaxial negative, and no pleochroism was observed; $X = Y = Z =$ colorless. Indices of refraction are α 1.580(1), β 1.588(1), and γ 1.593(1). The measured $2V$ is $74(1)^\circ$, and the calculated $2V$ is 76.3° . Dispersion is medium, $r < v$. Optic axes are oriented as $a \wedge Z = +50.5^\circ$, $b = Y$, $c \wedge X = +35^\circ$. The compatibility [$1 - (K_p/K_c)$] is equal to 0.012; thus the compatibility is superior.

CHEMICAL COMPOSITION

Over the last decade, numerous analyses of esperanzaite were undertaken by various methods, but, as is often the case, determination of the correct formula awaited the solution of the crystal structure. For this study, despite the previous analyses, new analyses were undertaken with the insight provided by knowledge of the atomic arrangement.

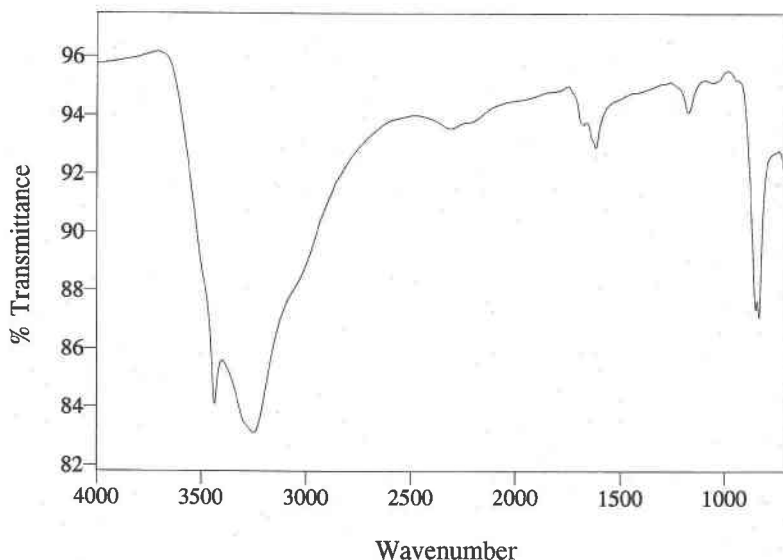


FIG. 1. Infrared spectrum of esperanzaitite.

Table 1 gives the results of the chemical analysis of esperanzaitite. Cations other than H were determined by electron microprobe, with standards as listed; H₂O was determined by Karl Fisher coulometric titration. Results of three electron-microprobe analyses of each of two grains were averaged to yield an empirical formula of Na_{0.68}Ca_{2.03}Al_{2.06}(AsO₄)[(As_{0.94}Zn_{0.07})O_{3.87}]

F_{4.00}(OH)•2.13(H₂O) or, ideally, NaCa₂Al₂(As⁵⁺O₄)₂F₄(OH)•2H₂O, on the basis of (O + F) = 15. As noted subsequently, the Na site is only partially occupied, explaining the disparity between the observed and ideal formulae.

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

Precession photographs of esperanzaitite reveal a cell with diffraction symbol $P2_1/m$; successful solution of the crystal structure revealed the correct space-group to be $P2_1/m$. Table 2 gives the crystal data and results of the structure refinement, and Table 3 lists the powder-diffraction pattern of esperanzaitite.

A crystal of esperanzaitite was mounted on a CAD4 single-crystal diffractometer. The unit cell was determined from least-squares refinement of the setting

TABLE 1. CHEMICAL COMPOSITION OF ESPERANZAITITE

Constituent	Proportion	Standard
As wt. %	26.50(37)	calcium fluorarsenate
Al	10.16(18)	synthetic corundum
Ca	14.83(15)	calcium fluorarsenate
Zn	0.70(5)	ZnO
Na	2.86(12)	albite
F	13.9(20)	fluorite
H ₂ O (titration)	8.65	
O (calc. by charge balance)	24.45	
TOTAL	102.15	

Empirical formula: Na_{0.68}Ca_{2.03}Al_{2.06}(AsO₄)[(As_{0.94}Zn_{0.07})O_{3.87}]F_{4.00}(OH)•2.13(H₂O)
Ideal formula, (O + F) = 15 atoms per formula unit on the basis of the structure solution: NaCa₂Al₂(As⁵⁺O₄)₂F₄(OH)•2H₂O

Chemical tests: Inductively coupled argon-plasma analysis yielded the following trace-element abundances (in ppm): Ba 2.4, Be 88, Cd 7.4, Cu 480, La 11, Li 42, Pb 210, Sb 13, Sc 25, Sn 230, Sr 25, Y 46, Yb 5.8, Zn 5900.

Operating conditions: ARL-SEM-Q microprobe, accelerating voltage 15 kV, beam current 10 nA, counting time 40 seconds. One standard deviation of least units cited in parentheses.

TABLE 2. CRYSTAL DATA AND CRYSTAL-STRUCTURE RESULTS FOR ESPERANZAITITE

Crystal size: 0.10 × 0.05 × 0.04 mm	Unit cell ($P2_1/m$):
Data-collection parameters:	a 9.687(5) Å
$0 < \theta < 30^\circ$; $+h, +k, \pm l$;	b 10.7379(6) Å
≤ 180 seconds	c 5.5523(7) Å
0:20 scans	β 105.32(1)°
Refinement results:	
$R_{\text{merge}} = 0.021$; $R = 0.032$;	$R_w = 0.037$; $R_{\text{all reflections}} = 0.073$
Goodness-of-fit = 1.858;	970 observations ($I > 4\sigma$),
122 variable parameters	$\Delta\rho$ (max, min), $\epsilon/\text{\AA}^3$, 0.73, -0.79

TABLE 3. POWDER-DIFFRACTION PATTERN OF ESPERANZAITTE

d_{obs} (Å)	$h k l$	d_{calc} (Å)	I_{obs}	I_{calc}
9.383	1 0 0	9.343	40	25.1
5.364	0 0 1	5.355	80	42.4
	0 2 0	5.369		50.5
4.796	0 1 1	4.792	80	100.0
3.930	1 1 1	3.905	20	52.0
3.801	0 2 1	3.791	80	94.3
3.527	2 2 0	3.524	90	27.4
3.272	2 2 $\bar{1}$	3.257	20	16.8
3.145	2 0 1	3.134	20	31.2
3.076	3 0 $\bar{1}$	3.067	20	0.2
2.966	1 3 $\bar{1}$	2.964	100	46.5
	3 1 $\bar{1}$	2.949		83.5
	0 3 1	2.976		37.4
2.844	2 3 0	2.841	2	1.3
2.700(b)	2 2 1	2.707	90	29.1
	0 0 2	2.678		27.9
	0 4 0	2.684		11.9
2.328	2 4 0	2.328	20	6.7
2.246	2 4 $\bar{1}$	2.245	60	27.8
2.203	1 2 2	2.199	20	46.0
2.146	0 3 2	2.144	20	2.5
2.101	2 0 2	2.096	20	11.8
1.820	5 2 $\bar{1}$	1.816	30	14.3
1.787	0 6 0	1.790	40	14.3
1.700	0 6 1	1.697	30	7.3

Ni-filtered Cu radiation, 45 kV, 12 mA, air, 5.3 hours, 114.6 mm Gandolfi camera, visual estimates of intensity, I_{calc} from crystal structure.

angles of 25 automatically centered reflections (Table 2). Intensity data were collected, and absorption was corrected using the Ψ -scan method. The atomic arrangement was successfully solved by direct methods as implemented in program MULTAN, coupled with difference-Fourier analysis. Hydroxyl groups, fluorine, and H₂O molecules were distinguished from oxygen atoms by examining bond-valence sums and distances to bonded cations. The refinement was undertaken using the *SDP for Windows* solution-refinement package (Frenz 1997). Scattering factors for neutral atoms were used, with corrections for anomalous dispersion; unit weights were assigned to all reflections with $I > 4\sigma_I$. The solution was begun and successfully completed in space group $P2_1/m$; the intensity distribution supported the centrosymmetric space-group, which was ultimately confirmed with the successful solution and refinement. Attempts at locating H atoms were unsuccessful.

Table 4 lists the positional parameters and isotropic B values for the atoms. Table 5 lists selected bond-lengths in esperanzaitte, and Table 6 lists the anisotropic displacement parameters for the atoms in esperanzaitte. Table 7 lists observed and calculated structure-factors, and Table 8 gives the bond-valence sums for all atoms in esperanzaitte. Tables 6 and 7 may be obtained from

TABLE 4. POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR ESPERANZAITTE

Atom	x	y	z	$B(\text{Å}^2)$
As1	0.0074(1)	1/4	0.1397(2)	0.67(1)
As2	0.54657(9)	1/4	0.8681(2)	0.65(1)
Ca	0.3555(1)	0.4175(1)	0.2602(2)	0.87(2)
Al	-0.2436(2)	0.4108(2)	0.2750(3)	0.71(3)
Na	0.1883(6)	1/4	-0.2949(9)	1.71(9)
F1	0.2191(4)	0.4361(4)	-0.1665(7)	1.34(7)
F2	0.4038(4)	0.5319(4)	0.6411(6)	1.10(6)
OH	0.7260(6)	1/4	0.382(1)	0.8(1)
Ow	0.1511(5)	0.5406(4)	0.3739(8)	1.13(8)
O1	0.1848(6)	1/4	0.267(1)	1.2(1)
O2	-0.0601(4)	0.3748(4)	0.2470(8)	1.15(8)
O3	0.4242(6)	1/4	1.030(1)	0.8(1)
O4	0.4710(7)	1/4	0.564(1)	1.2(1)
O5	0.3476(4)	0.6224(5)	0.0582(8)	0.92(7)
O6	-0.0320(7)	1/4	-0.172(1)	1.4(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2 * \beta_{11} + b^2 * \beta_{22} + c^2 * \beta_{33} + \beta_{12} * ab(\cos \gamma) + \beta_{13} * ac(\cos \beta) + \beta_{23} * bc(\cos \alpha)]$.

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DESCRIPTION OF THE ATOMIC ARRANGEMENT

In esperanzaitte, like many seemingly complex minerals, the atomic arrangement is clarified by viewing the structure as packing of its constituent polyhedra. The Fundamental Building Block (*FBB*) is formed by pack-

TABLE 5. ESPERANZAITTE: BOND DISTANCES (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
As1-	O1	1.676(6) Å	Al-	F1	1.788(4)
	O2 ($\times 2$)	1.669(5)		F2	1.840(4)
	O6	1.672(6)		OH	1.874(3)
Mean		1.672		Ow	1.988(4)
				O2	1.866(5)
As2-	O3	1.668(7)		O5	1.892(4)
	O4	1.654(6)	Mean		1.875
	O5 ($\times 2$)	1.696(4)			
Mean		1.679	Na-	F1 ($\times 2$)	2.116(4)
				O6	2.405(9)
Ca-	F1	2.397(4)		O1	2.424(9)
	F2	2.314(4)		O3	2.510(7)
	F2	2.383(4)	Mean		2.314
	Ow	2.594(5)			
	O1	2.451(5)			
	O3	2.398(5)			
	O4	2.516(4)			
	O5	2.461(5)			
Mean		2.439			

ing of octahedra and tetrahedra, which are hosted by interstitial cations with irregular coordination polyhedra.

AsO₄ tetrahedra and octahedrally coordinated Al atoms [AlF₂O₂(OH)(Ow)] form the *FBB* in esperanzaité. The *FBB* is comprised of [001] stacks of heteropolyhedral tetramers; the tetramers are formed of two arsenate tetrahedra and two Al octahedra (Fig. 2). Within the tetramer, the Al octahedra share three corners. Each octahedron shares OH with a neighboring Al octahedron, and also shares O2 with one AsO₄ group and O5 with the other arsenate group.

Figure 2 depicts the stacking of the *FBB* tetramers in the cell. The stacks of tetramers are linked laterally by irregular Na ϕ ₅ and Ca ϕ ₈ polyhedra (ϕ : unspecified anion), which also serve to link adjacent tetramers within a chain. The Na and Ca polyhedra polymerize to form (100) ribbons that weave through the *FBB*, linking the stacks of tetramers.

In all analytical datasets, Na was found to occur in amounts significantly less than one atom per formula unit, a fact that led to confusion in early attempts to calculate the formula of esperanzaité. The solution of the atomic arrangement confirmed that indeed the Na site is only partially occupied, with 86% occupancy in the crystal chosen for the structure refinement, and even less in the crystals submitted for chemical analysis (average 68%). However, the structural reason for partial occupancy is not clear.

Bond-valence sums are given in Table 8. As shown there, anion assignments are easily distinguished on the

TABLE 8. BOND-VALENCE SUMS FOR ATOMS IN ESPERANZAITÉ (VALENCE UNITS)

	As1	As2	Al	Ca	Na	Sum
O1	1.28	---	---	0.27($\times 2^-$)	0.19	2.01
O2	1.30($\times 21$)	---	0.56	---	---	1.86
O3	---	1.29	---	0.31	0.15	1.75
O4	---	1.36	---	0.23($\times 2^-$)	---	1.82
O5	---	1.22($\times 21$)	0.52	0.26	---	2.00
O6	1.29	---	---	---	0.19	1.48
OH	---	---	0.55($\times 2^-$)	---	---	1.10
Ow	---	---	0.40	0.18	---	0.58
F1	---	---	0.52	0.22	0.31($\times 21$)	1.05
F2	---	---	0.45	0.23, 0.28	---	0.96
Sum	5.17	5.09	3.00	1.98	1.15	

basis of bond valence, except for O6 and Ow; the former is underbonded (bond valence = 1.48 valence units, *vu*) and the latter overbonded (bond valence = 0.58 *vu*). There is a close contact between O6 and Ow, each O6 atom having two Ow atoms 2.64 Å distant, with a Ow–O6–Ow angle of 117°. Such near-tetrahedral angles suggest that significant hydrogen bonding (~ 0.3 *vu*/H atom) is contributed to O6 from Ow (Chiari & Ferraris 1982), thus balancing the charge among the Ow–O6–Ow system.

ACKNOWLEDGEMENTS

Not long before his death, Gene Foord contacted me (JMH) to ask if I would attempt to solve the atomic arrangement of esperanzaité, and fortunately the attempts were successful. As I put this manuscript together, I hope I have included authors who contributed significantly to the project, and I apologize to those who perhaps should have been included but were not; unfortunately Gene was not here to guide me.

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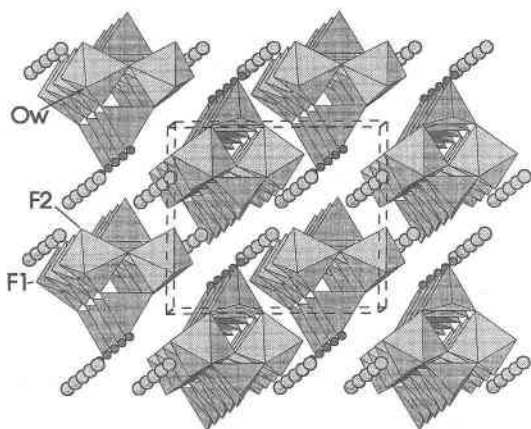


FIG. 2. Arrangement of *FBB* tetramers in esperanzaité. Unit cell is depicted with *b* horizontal and *a* vertical. Na (smaller) and Ca (larger) atoms are depicted. Hydroxyl groups link adjacent Al octahedra, and Ow, F1 and F2 are marked.

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